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PROMISING HIGH-TEMPERATURE COMPOSITE MATERIALS AND COATINGS FOR AEROSPACE TECHNOLOGY

S. St. Solntsev,[1] D. V. Grashchenkov,[1] and S. A. Evdokimov[1]

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The problems of developing high-temperature composite materials for aerospace engineering and methods for obtaining them as well as their advantages over the technologies widely used abroad are examined.

Key words: high-temperature composite material, antioxidative coating, heat-resistance, promising aerospace technology.

In order to develop promising new-generation aerospace technology, propulsion and ground-based gas-turbine power plants with 40 – 60% greater efficiency, 1.5 – 2.0 times higher reliability and longer service life, making it possible to reduce the emission of pollutants it is necessary to increase the gas temperatures in front of the turbine and, correspondingly, develop light, strong, rigid, corrosion-resistant materials operating at temperatures above 1500°C [1, 2].

Ceramic composite materials are distinguished by a complex of properties not previously attained for other materials and have a number of advantages over metal alloys, viz., the capability of maintaining properties in an oxidative medium at temperatures above 1200°C, good durability, excellent corrosion properties and low density and low thermal expansion, which makes them irreplaceable for use in heat-intensive units and parts in promising manufactured articles, under the conditions of oxidative media at high temperatures [3, 4].

Ceramic composite materials SiC_{fib}/SiC (based on a SiC matrix reinforced with fabric or continuous fibers SiC_{fib}) have low density (about 30 – 50% of the density of metals) and low linear thermal expansion coefficient (about 60% of the CLTE of metals) and can potentially operate at temperatures to 1600 – 1650°C [5].

A comparative assessment of the levels of technological development has revealed that foreign technologies for obtaining ceramic composite materials (CCM) by deposition from the gas phase in order to obtain matrices based on SiC require complex, special equipment and they are distinguished by high costs due to the high energy-intensiveness of the processes (technological operations requiring up to six months) and by the use of expensive continuous SiC fibers as reinforcing elements. At the same time, analysis of the working characteristics of the best foreign ceramic composite materials (CCM) reinforced with fibers such as Hi-Nicalon and Sylramic showed that the working temperature of SiC–SiC composites does not exceed 1400 – 1450°C in an oxidative medium [6].

A qualitative leap in the development of high-temperature materials science is impossible without new unconventional approaches to the development of materials and structures from them and can be accomplished only with the development of profitable processes for obtaining ceramic composite materials, including sol-gel technology, nanotechnology and other advanced technological solutions based on increasing the reactivity of structural elements above that of conventional materials, which will make it possible to decrease the energy-intensiveness of the technological operations in the high-temperature processes involved in the synthesis of CCM.

An advantage of the sol-gel method over conventional methods of obtaining materials is that it makes it possible to secure high-purity initial components and a homogeneous final product (CCM), regulate the microstructure of the materials at the initial stage of the process; in addition, unlike the methods of chemical precipitation or infiltration from the gas or vapor phase it does not require complicated equipment

[1] All-Russia Research Institute of Aviation Materials (VIAM), State Scientific Center of the Russian Federation, Moscow, Russia (e-mail: admin@viam.ru).

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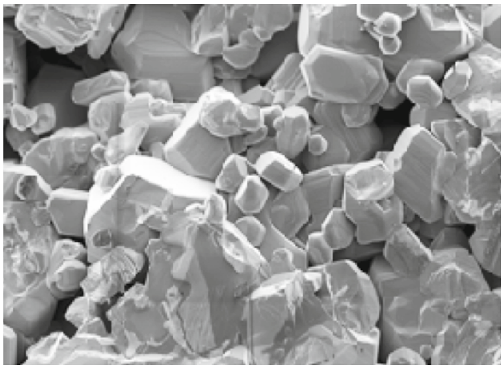

Fig. 1. Microstructure of a sample of a composite material of the type SiC–SiC.

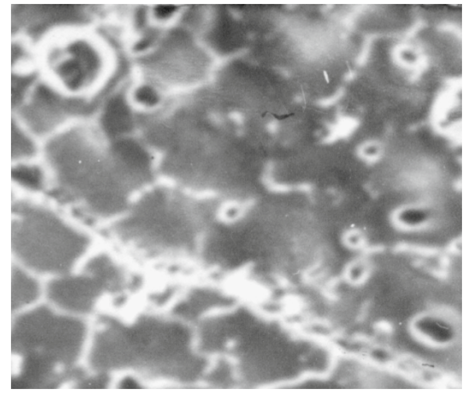

Fig. 2. Self-healing of a microcrack on the surface of CCM.

and differs by lower energy consumption in the process operations [7, 8].

The main process having the greatest effect on the structure and properties of the ceramic composite material of the type SiC–SiC developed at VIAM is high-temperature synthesis where physical (evaporation-condensation, recrystallization via a liquid phase, diffusion-viscous flow and others) and chemical processes leading to the formation of a matrix and the composite as a whole occur [9].

High-temperature synthesis results in the directed formation in a composite on the micro- and nanolevels of a continuous silicon-carbide framework, where the ordering particles are incorporated into the structure of the matrix, formed as a result of high-temperature synthesis from the initial components. Microstructural analysis revealed an embedded heterogeneous polycrystalline structure with very low closed porosity and crystal grains mainly 0.1 – 5 μm in size. The microstructure of a sample of a SiC–SiC ceramic composite material is presented in Fig. 1.

High-temperature chemical synthesis makes it possible to purposefully change the properties of CCM, such as density, porosity, strength and others, by regulating the structure [10].

A distinguishing feature of a ceramic composite material of the type SiC–SiC is high stability (in contrast to the conventional monolithic ceramic) during cycling heating in the combustion products of fuel in the regime 1550 (1600)°C ⇄ 800°C with more than 10,000 cycles (1 cycle = 1 min) without failure.

The new ceramic composite material is also distinguished by very high resistance to oxidation. At temperatures to 1650°C there is no mass loss for a long time; there is a mass increment of no more than 5%. This behavior of the material is associated with the formation of a thin amorphous silica film on the surfaces of grains in an oxidative medium that blocks oxygen diffusion into the material and makes possible self-healing of different defects by blocking pores, cracks and so forth. The microstructure of CCM with a self-healed microcrack is presented in Fig. 2.

Self-healing of a material during operation keeps the mechanical characteristics at the initial level and improves the protective characteristics at high temperatures.

Technical Characteristics of SiC–SiC Ceramic Composite Material

Working temperature, °C	1550 – 1650
Medium	Oxidative, products of fuel combustion
Density, g/cm^3	2.5 – 2.9
Porosity, %	5 – 8
Ultimate strength in four-point bending, MPa, at temperature:	
20°C	180 – 200
1550°C	180 – 200
Thermal conductivity, W/(m · K), at temperature:	
20°C	5 – 50
1000°C	30 – 35
CLTE at 20 – 1550°C, 1×10^{-6} K^{-1}	4.9 – 5.2

The technology for fabricating parts (segments) of a combustion chamber for promising propulsion plants from a composite material based on an oxygen-free ceramic of the type SiC–SiC was developed experimentally. Segments made from SiC–SiC composite material are presented in Fig. 3.

The possibility of developing a secondary framework-like structure in a SiC–SiC CCM was shown in work performed jointly with the N. S. Kurnakov Institute of General and Inorganic Chemistry and the D. I. Mendeleev Russian Chemical Technology University.

The choice of starting reagents was validated and a hybrid method combining the sol-gel technology and high-temperature chemistry in a gas medium (carbothermal synthesis) was used to synthesize nanosize SiC in the form of 20 – 50 nm particles, whiskers and fibers smaller than 50 nm in diameter and 200 – 400 nm long (l/d = 5 – 60) in the pores of the ceramic composite material (Fig. 4).

At the present time carbon-containing composite materials (carbon-carbon type C/C and carbon-ceramic type C/SiC)

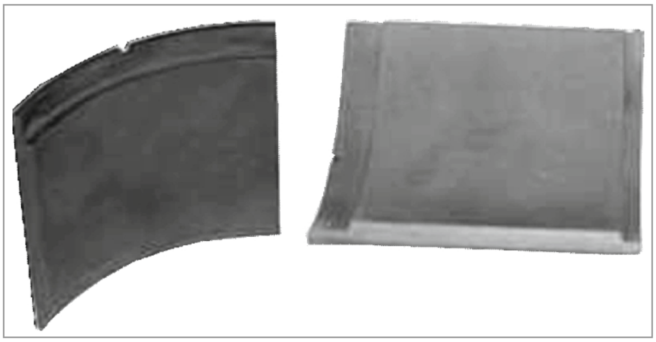

Fig. 3. Segments for a promising combustion chamber made of SiC–SiC CCM.

distinguished by low density and high strength at high temperatures are regarded as the most promising materials for the most heat-loaded elements of structures designed in the aerospace technology under development, including hypersonic aircraft. However, starting at 400°C carbon actively oxidizes, which results in degradation of the material used for high-temperature units and parts.

To secure serviceability and efficient use of carbon-containing composites in an oxidative medium during fabrication of heat-loaded units and parts it is necessary to use a complex system of protection from oxidation, which prevents carbon from interacting with the oxygen in gas flow and the surrounding environment and performs the functions of barrier, erosion-resistance and anti-oxidant and other coatings.

The difficulty in developing long-life anti-oxidant coatings is that at high temperatures the initial refractory compounds present in the coatings undergo irreversible change with time and transform into the corresponding oxides which show high diffusion permeability for the oxygen in air [11].

High-temperature coatings based on silicon carbide are characterized by the fact that at high temperatures during the interaction with the oxygen in the ambient environment a liquid phase based on silicon dioxide SiO_2 forms on the surface of the coating, which seals the surface and retards the interaction of the components of the coating with oxygen. Because the CLTE of the protected composite material is different from that of the coating (or for other reasons) microcracks can form in the coating during operation [9].

It is well known that an RCC coating based on silicon carbide SiC, used at temperatures to 1650°C in the space-shuttle parts to protect the nose cone and the front edges of the wings, is serviceable for 30 – 40 h only with regular maintenance by permeation with tetraethyl orthosilicate.

In our country development work on coatings for carbon-containing composites was performed in connection with the development of the Buran reusable orbital space vehicle. The domestic analog is the M-46 coating, which was developed for protecting the leading edges of the wings made of carbon-carbon composite and had a service life of one flight (20 – 25 min).

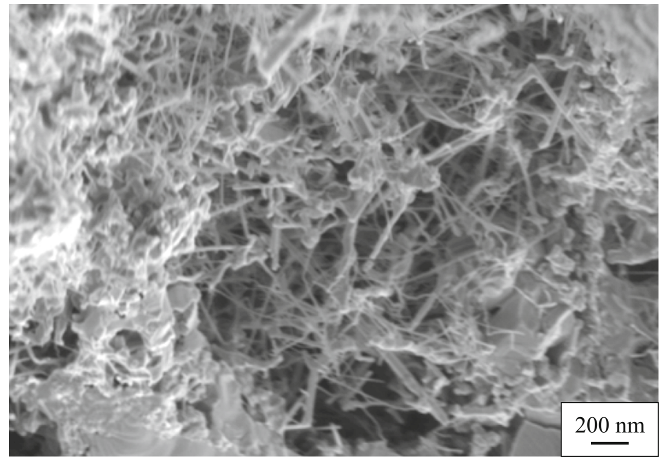

Fig. 4. Microstructure of a sample (filling of the pores with nanosize SiC is evident).

The conventional silicon-containing components — silicon carbide and silicon nitride, which is the basis for many protective coatings, and SiO_2 donors (glass phase) — oxidize intensely at 1800°C, resulting in the formation of very volatile compounds that destroy the integrity of the coating, causing it to degrade.

The following basic requirements for ceramic composite coatings capable of operating at temperatures 1650 – 1800°C and higher have been formulated:

1) physical-chemical compatibility and CLTE matching with the protected material;

2) thermal and chemical stability of the components;

3) erosion resistance;

4) presence of self-healing during operation.

The phase transformations occurring in ceramic coatings are controlled and monitored by varying the parameters of the production process, which makes it possible to secure a prescribed service life in the presence of erosion due to high-temperature flows.

A multilevel system for protecting carbon-ceramic composite materials can be thought of as consisting of several layers each of which carries its own functional load and in which the content of one component or another is predominant. It is precisely the silicon-containing components that are the sources of chemical interactions in the layer of a coating, and they promote self-healing of defects in the layer. The difficulty of the scientific-technical problem lies in developing methods and technology for obtaining new unconventional compounds making it possible to develop self-healing coating compositions on their basis with working temperature to 1800°C and higher.

A technology for high-temperature chemical synthesis of ceramic compositions based on controllable interaction of the initial components, including silicon- and boron-containing components, in a high-temperature heating regime in the presence of oxygen from air, was developed as the most

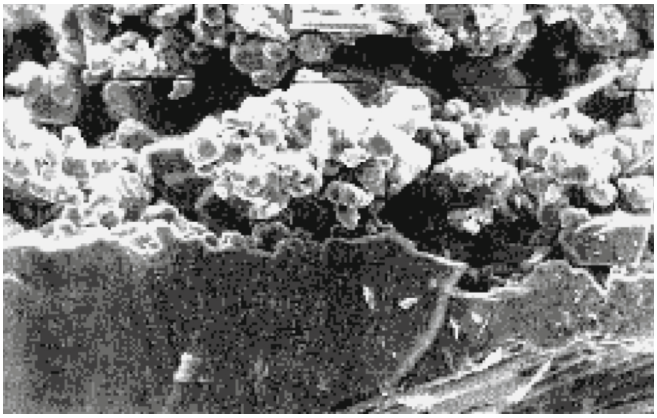

Fig. 5. Microstructure of an antioxidant coating; × 600.

promising direction for increasing the effectiveness of the protective action of anti-oxidant coatings.

High-temperature coating systems for protection from oxidation and degradation of carbon-ceramic composite materials at temperature up to 2000°C have been developed at VIAM.

The protective action of such coatings is due to the formation on the surface of the substrate of a dense gas-impermeable layer, formed as a result of the chemical interaction of the initial components and intermediate products on heating in the presence of oxygen from the ambient air.

The high-temperature synthesis technology has the following advantages:

first, the possibility of obtaining ceramic composite coatings at temperatures 300 – 500°C lower than the operating temperature;

second, the possibility of regulating the chemical composition of a coating in wide range depending on the required working temperature by developing new compositions with the required properties, differing from those of the initial components of the coating (for example, high heat-resistance), directly on the protected ceramic composite materials in an oxidative medium;

third, a significant reduction in the time (instead of duration, which could be several months) required to obtain the coating using less complicated, expensive equipment; the possibility of self-healing of ceramic compositions or formation of a glass phase with different heat-resistance during heat-treatment that is capable of localizing defects in the form of pores and cracks by plugging.

The novelty of the antioxidant ceramic composite systems developed at VIAM lies in the fact that the production of the protective layers and their serviceability at temperature to 2000°C are attained by means of chemical interaction of the components of the coating and oxygen from the ambient environment. In addition, the oxygen is retained in all outer layers of the coating, which secures multilevel protection of the carbon material. A viscous-flow phase, which heals cracks in the coating, can form at the same time [12].

The protective action of the coating is determined by the processes occurring at the interfaces between the ambient gas medium and the surface of the coating, the interlayer boundaries, and between the coating and the substrate.

A layer-by-layer x-ray phase analysis and an electron probe scanned over the surface and sections of a coating showed that a coating consists of a refractory matrix and a glass phase, which fills the interphase region along grain boundaries, pore, cracks and capillary channels. The microstructure of an antioxidant coating is shown in Fig. 5.

The surface layer of the glass phase serves as a barrier in the path of oxygen from the gas phase into the interior layers of the coating. The oxide compounds have their maximum concentration near the outer interface with the gas medium. As result of reactions several layers differing by the chemical and phase compositions and the thermochemical stability form in the coating. In each layer the content of certain components is predominant. Regulation of the chemical and phase transformation processes in the coatings makes it possible to secure a prescribed service life and working temperature and impart functional properties such as erosion resistance, radiation power, catalyticity and others. The working temperature and heat-resistance of the coating increase with the content of the refractory and glass-forming compounds. The effectiveness of the protective action of the coating also depends on the possibility of continual additional formation of new phases owing to the oxidation of the initial components.

The new high-temperature coating systems developed at VIAM open the prospects for practical applications of unique carbon-ceramic composite materials in an oxidative medium right up to 2000°C in aerospace technology, power generation, metallurgy and machines.

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